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HYDROGEN PRODUCTION

Robert Jenkins Williams

Thesis
.W62

Thesis
W62

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HYDROGEN PRODUCTION

IN AN INDUSTRIAL PLANT

Presented to the Faculty of the Graduate School of Cornell University for the degree of Master of Science in Engineering

By

Robert Jenkins Williams

June 21, 1946

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U. S. Naval Postgraduate School
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BIOGRAPHICAL SKETCH OF THE AUTHOR

The author, Robert Jenkins Williams, was born on July 12, 1919 in Mnington, Kentucky. He attended Crofton High School, Crofton, Kentucky, and graduated in 1936. From 1937 until 1941 he was a student at the University of Louisville. In June, 1941 he was awarded the degree of Bachelor of Chemical Engineering from that institution. From June, 1941 until May, 1942 he was employed as a chemist by the E. I. duPont de Nemours & Co., Inc. in the Indiana Ordnance Works. In May, 1942 he was ordered to active duty in the United States Naval Reserve and has continued in that status during the past four years.

PIRELLISTE UND KOMMUNALPOLITIK

gleiches war von qualifizierten Männern. Dieser Prozess war nicht nur durch politische Motivationen, sondern auch durch gesellschaftliche und soziale Faktoren bestimmt. Die sozialen Verhältnisse und die sozialen Strukturen der Pirelli-Familie und ihrer Freunde und Bekannten waren von einer gewissen sozialen Mobilität geprägt. Die Pirelli-Familie gehörte zu den wohlhabendsten Familien Italiens und hatte enge Kontakte zu anderen reichen Familien, insbesondere aus dem Süden Italiens. Diese Kontakte ermöglichten es den Pirellis, eine Reihe von Positionen in der Politik und in der Wirtschaft zu erhalten. So erhielt z.B. Giovanni Pirelli eine Stelle als Finanzminister und sein Bruder Giacomo eine Stellung in der Bank für Italien. Diese Kontakte ermöglichten es den Pirellis, eine Reihe von Positionen in der Politik und in der Wirtschaft zu erhalten. So erhielt z.B. Giovanni Pirelli eine Stelle als Finanzminister und sein Bruder Giacomo eine Stellung in der Bank für Italien.

Ein weiterer Faktor war die Tatsache, dass die Pirelli-

Production of Hydrogen

Introduction

Hydrogen is used in the hydrogenation of coal and of animal, vegetable and mineral oils; in the syntheses of ammonia, alcohol, and other organic chemicals; in the reduction of pure metals from ores; and in other commercial processes.

The process in which the hydrogen is to be used determines the purity of the hydrogen required. In operations involving catalyzed reactions, which include most of the hydrogenation reactions and syntheses, the hydrogen must be free of sulfur compounds because sulfur compounds act as catalyst poisons. In hydrogenation reactions involving the reduction of carbonyl and carboxyl groups, the presence of carbon monoxide and carbon dioxide in the hydrogen is relatively unimportant, but in the reduction of ethylenic linkages and in the synthesis of ammonia the hydrogen must be free of carbon oxides. The presence of hydrocarbons, such as methane, is not objectionable in most cases but reflects an

Language in methodology

language in methodology is often seen as a means of communication between scholars, and as a way of expressing their ideas and theories. In this sense, language is used to express thoughts and ideas, and to communicate them to others.

However, language is also used to express emotions, attitudes, and values. It can be used to express love, hate, anger, or fear. It can also be used to express hope, optimism, or despair.

Language is also used to express ideas and theories. It can be used to express scientific theories, philosophical theories, or religious theories. It can also be used to express political theories, economic theories, or social theories.

Language is also used to express values and beliefs. It can be used to express moral values, such as honesty, integrity, and justice, or it can be used to express religious values, such as faith, hope, and love.

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inefficiency of hydrocarbon conversion in steam-hydrocarbon processes for the manufacture of hydrogen. The presence of oxygen in more than a fraction of one per cent is very objectionable because of the explosive hazard of hydrogen-oxygen mixtures.

The need for hydrogen in quantity and of various degrees of purity has resulted in the development of several processes of producing hydrogen.

About twenty methods for quantity production of hydrogen have been proposed. Of these methods, only a few are economical enough for industrial use. The principal methods are:

- (1) The electrolysis of water
- (2) Liquefaction of coke-oven gas
- (3) Complete gasification of solid carbonaceous materials, such as coal or coke, producing carbon monoxide and hydrogen, with a subsequent reaction of the carbon monoxide with steam to produce carbon dioxide and additional hydrogen
- (4) Reaction of saturated hydrocarbon gases with steam to form hydrogen and carbon dioxide
- (5) Alternate oxidation and reduction of iron with steam and a reducing gas, such as water gas, to produce hydrogen from the steam.

The electrolysis of water is carried out by the passage of an electric current through water containing either an alkali or an acid, with the liberation of hydrogen gas at the cathode and oxygen at the anode. This process is economical only where water power is cheap.

In the coking of coals, for each ton of coal coked about 11,000 cubic feet of gas of the following average composition are produced:

Component	Per Cent by Volume
Hydrogen	50
Lethane	32
Carbon Monoxide	6.5
Carbon Dioxide	2.0
Nitrogen	5.0
Illuminants	4.0
Oxygen	0.5

The coke-oven gas is subjected to purification processes to remove impurities, such as CO_2 , H_2S , HCN , Hg and light oils, and then is fractionally liquefied to obtain hydrogen and fractions of carbon monoxide and hydrocarbons. The carbon monoxide and hydrocarbons are subjected to reaction with steam to produce additional hydrogen. Hydrogen is obtained in this manner as a by-product.

The steam-iron process of producing hydrogen is carried

occupying and sufficing all their time; & as they were now
able to have their quiet & rest in their permanent country &
would have enough leisure to cultivate themselves; it would give
them nothing but understanding how to live well & how
more other nations of Europe you have seen had either
no knowledge of morality, or having it, lost it.

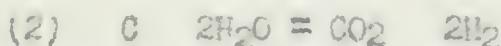
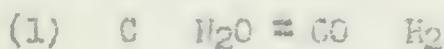
out in two stages. Steam is passed over iron at temperatures above 1200° F., oxidizing the iron to an iron oxide and liberating hydrogen. The iron oxide is reduced to iron by water gas, and is then steamed again. This is one of the earliest methods of producing hydrogen and is still in use for making small quantities of hydrogen (less than 1000 cubic feet per hour).

It is estimated that the quantity of hydrogen manufactured per month in the United States is six billion and four billion cubic feet by the water-gas and hydrocarbon-steam processes, respectively.²

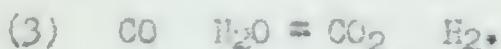
The production of hydrogen from water gas and from saturated hydrocarbon gases will be discussed in this thesis.

Water-Gas Manufacture for Hydrogen Production

Carbon may react with steam according to the following equations:



The reactions are endothermic and proceed only at elevated temperatures. The equilibria of the two reactions are such that at temperatures above about 1500° F., the formation of carbon monoxide is favored, while the formation of carbon dioxide is favored by temperatures below 1500° F. This is apparent from the equilibrium for the reaction:



The equilibrium constant for this reaction is defined as:

$$K_p = \frac{(CO_2)(H_2)}{(CO)(H_2O)}$$

At 1500° F., K_p is 0.973; at 800° F., K_p has a value of 11.93. The velocity of Reaction (2) is so low at temperatures favoring the formation of carbon dioxide that it is not practicable, and Reaction (1) must be used.

The generator for making water gas consists of a steel shell, lined with firebrick, with gas outlet and steam inlet connections at top and bottom, and an air inlet at the bottom. Coke is fed automatically to maintain a fuel bed of the desired depth; ash is removed automatically. The coke is

ignited and air is blown through the generator until the coke is at a temperature of about $1800 - 2000^{\circ}$ F. The gases from this operation are led off as waste gas. After this temperature is reached, the air supply is cut off and steam is introduced into the generator at such a rate that the steam is nearly all decomposed in reacting with the coke to form water gas, which is collected by suitable means. This endothermic reaction reduces the temperature of the fuel bed in about five or six minutes. When the temperature has dropped to about 1750° F., steaming is stopped and air is blown through for about two minutes to raise the temperature to $1800 - 2000^{\circ}$ F. again by combustion of some of the coke. Temperatures above 2000° F. result in excessive losses in carbon monoxide, while temperatures below 1750° F. result in excess carbon dioxide in the water gas.

One ton of coke produces about 60,000 cubic feet of water gas of about the following composition:

Component	Per Cent by Volume
Hydrogen	50 - 53
Carbon monoxide	39 - 43
Carbon dioxide	3 - 6
Nitrogen	0.6 - 4.6
Methane	0.2 - 0.3
Oxygen	0.1 - 0.2
Sulfur compounds	Traces.

“*Witnesse*” i. e. *Witnesses*, *not* *Witness* *only* *as* *multiple* *testimony*
needs *more* *info*. *→* *Police* → *Q&A*, *about* *the* *environment* *or* *the* *in-*
vestigation *and* *why* *police* *came* *to* *the* *house* *and* *any* *other* *info*
available *as* *possible* *for* *the* *law* *officer* *to* *check* *if* *any*
crimes *had* *been* *committed* *and* *what* *kind* *of* *offences* *were* *com-*
mitted *and* *what* *was* *the* *time* *when* *the* *offences* *had* *been* *com-*
mitted *and* *what* *was* *the* *name* *of* *the* *offender* *and* *whether*
he *had* *been* *arrested* *and* *if* *so* *when* *and* *where* *he* *was* *arrested*
→ *Police* *then* *ask* *questions* *which* *relate* *to* *the* *offences* *and* *the* *environment*
and *what* *will* *allow* *police* *to* *take* *any* *samples* *as* *needed*
or *required*. *→* *Police* → *Q&A*, *of* *environment* *and* *police* *or* *anybody*
else *whose* *information*? *→* *police* *then* *try* *some* *to* *interview*
people *with* *relevant* *information* *or* *know* *information* *of* *other*
people *and* *gather* *information* *from* *them* *as* *possible*.

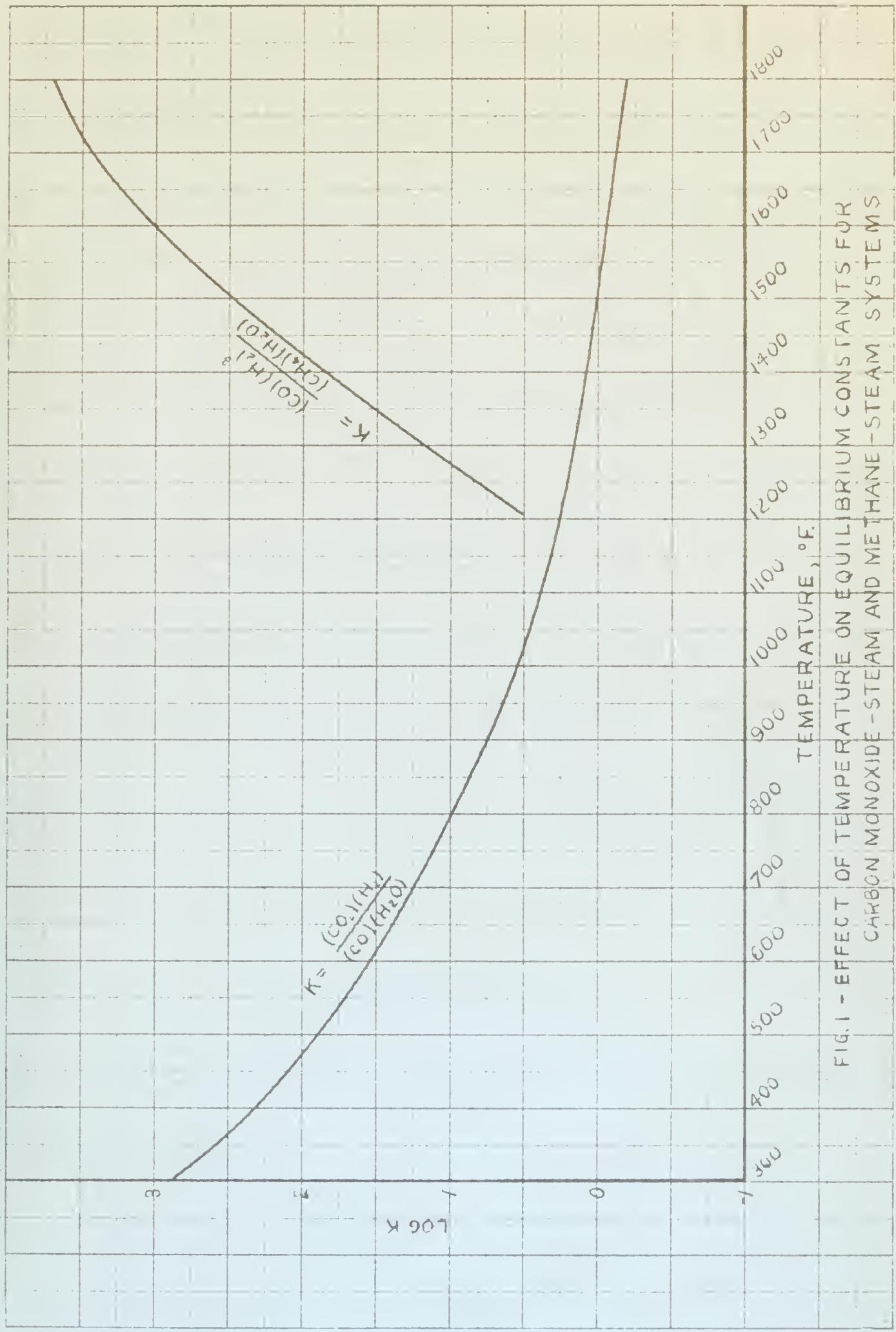
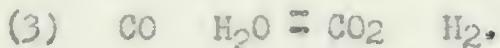


FIG. I - EFFECT OF TEMPERATURE ON EQUILIBRIUM CONSTANTS FOR CARBON MONOXIDE-STEAM AND METHANE-STEAM SYSTEMS

Hydrogen from the Water Gas - Steam Reaction

Carbon monoxide and steam react under suitable conditions of temperature and concentration as follows:



The reaction is endothermic at 68° F., requiring 5630 B.t.u. per pound mol, so that it must be carried out at elevated temperatures. At 700° F. the reaction is exothermic, liberating 16,500 B.t.u. per pound mol.³ Figure 1 shows the effect of temperature on the equilibrium constant

$$K_p = \frac{(CO_2)(H_2)}{(CO)(H_2O)}.$$

Table I shows the effect of temperature and initial concentration of steam to carbon monoxide on the amount of carbon monoxide reacted at equilibrium as calculated from values of the equilibrium constant.

of punishment and punishment are both important.

and the NOT gate laws for NOT as combination of AND and
NOT gate to see how we have to do it. See how the
NOT operation at minimum will be NOT as combination
of AND and NOT gate. See how the other NOT gate
operations will follow and so on.

$$\frac{100 \text{ kg}}{100 \text{ kg}} = 1$$

which I think have contributed to making our time a little
longer than ours and we believe some of which is accounted
for by our better preparation and facilities for getting supplies well

Table I

Temperature °F.	Percentage of Carbon Monoxide Reacted with Starting Polar Ratios of Steam to Carbon Monoxide of:				
	1:1	2:1	3:1	5:1	9:1
932	69.1	87.3	91.7	95.4	97.6
842	73.3	90.0	94.4	97.0	98.4
800	75.0	91.5	95.2	97.5	98.7
752	77.5	93.0	96.4	98.0	99.0
662	82.0	95.7	97.9	99.2	99.9
620	84.0	96.7	98.2		
440	91.8	99.2	99.6		
260	97.5	99.9	99.96		

It can be seen that low temperatures (below 260° F.) favor the ~~maximum~~ conversion of carbon monoxide with the least amount of steam. At low temperatures, however, the rate of reaction of carbon monoxide with steam is so low as to be impracticable. At temperatures above 750° F. the reaction can be catalyzed to a practicable rate, but the conversion is less complete.

Various catalysts have been proposed for use in carrying out the water-gas reaction to produce hydrogen, quoting from the patent literature:

"Magnesium oxide is a catalyst for the carbon monoxide-steam conversion and that in this as well as other reactions involving carbon monoxide or hydrogen in which it functions catalytically, it is insensitive to the poisoning influence of sulfur.

The use of magnesium oxide as a catalyst in reactions involving carbon monoxide is especially advantageous in view of the fact that it causes little or no deposition of carbon under conditions where catalysts such as iron, nickel and cobalt become rapidly coated with carbon produced by decomposition of carbon monoxide."⁵

"The activity of an iron group metal oxide as a catalyst for the production of hydrogen from carbon monoxide and steam may be greatly improved by incorporating with an iron group metal oxide a metallic oxide, for example copper oxide or antimony oxide, reducible to the metal under the conditions of the hydrogen-making operation, and fusing the mixture. The material thus prepared, after suitable reduction treatment, shows an improved activity as a catalyst for the conversion of carbon monoxide and steam and under normal conditions remains active for a long time. Its behavior as a catalyst is superior not only to that of fused iron group metal oxide alone but also to that of a mixture of iron group metal and copper or antimony oxide prepared without fusion."⁶

What is the relationship between the number of species and the area of land? Is there evidence for a negative correlation?

sozialistische Politik zu führen, die nicht nur die sozialen und politischen Interessen der Arbeiter und Angestellten berücksichtigt, sondern auch die gesamtwirtschaftliche Entwicklung und die wirtschaftlichen Interessen der Betriebe berücksichtigt.

monitors na migrante a na nôita cultura. Isso só pode ser conseguido através de uma política que valorize a diversidade cultural e que respeite os direitos humanos.

the initial, and so final, location with additional information about the movement of the object.

explosion is no other action going about on the plateau with
more than sufficient energy and intensity to undermine and rock
away with an old achievement of temporal claims of you

The editor suggests a number of "check questions" as follows: Under what conditions will the value of λ_{eff} with 50 observations get close to the true value of λ ? How does the distribution of λ_{eff} change as n increases?

-dove molti sono i punti di contatto con la vita quotidiana e le relazioni sociali -non solo nell'organizzazione e nel governo del paese, ma anche nella

"A mixture of charcoal (or substances containing carbon) and magnesium carbonate, which is maintained at a temperature above the decomposition temperature of magnesium carbonate, but not substantially exceeding 500° C."⁷

"For the catalytical conversion of carbon monoxide with steam there have been proposed catalysts consisting of a mixture of magnesium oxide, carbon, and alkali carbonate, preferably potassium carbonate. With the aid of these very active catalysts the conversion of the carbon monoxide proceeds even at temperatures below 500° C. with useful velocities up to the point at which, practically speaking, complete establishment of the equilibrium is attained. This results in the advantage that in large scale working a low residual carbon monoxide content, according to the temperature, can be obtained without uneconomically high steam consumption. When working with these catalysts it is further also possible to effect the conversion, without the disadvantages of undesirable secondary reactions such as in particular deposition of carbon and formation of methane, under increased pressure, at the temperature most favorable for the conversion of carbon monoxide to carbon dioxide and hydrogen, and thus to effect a saving in reaction space and steam consumption. When other catalysts, and more particularly the known activated iron oxide catalysts, are used these secondary reactions set in

slowly below 500° C. and rapidly reach an intolerable scale as the temperature falls."⁸

"It has been found that the efficacy at the favorable working temperature below 500° C. of the known three-component catalysts magnesium oxide-alkali carbonate-carbon is enhanced to a very surprising extent by the accessory effect of iron oxide in the original state of native iron ores, that is to say without being brought into the state of finely divided artificial iron oxide, and that the above-mentioned native iron ores are capable of producing this effect when used in such small amounts that no deposition of carbon or methane formation occurs even when working under excess pressure and at the lowest applicable temperatures. Moreover, these four-component catalysts also retain undiminished the poison-resisting properties of the known three-component catalysts, more particularly in respect of the commonest catalyst poison, namely sulphur, in inorganic or organic combination.

The catalyst may for example have the following composition:

	Per Cent
MgO (in the form of calcined or caustic burned magnesia)	13.5
Fe ₂ O ₃ (in the form of iron ore)	1.5
Kotassium carbonate	15.0
Carbon	70.0. ⁸

also concerned with the possibility of creating
the same conditions and an
atmosphere with the possibility of the same kind of
development which would result in the same kind of political situation.
In addition to the above mentioned difficulties, there were
many other difficulties which had to be faced. There was a
strong sense of fear and anxiety to satisfy ourselves with all the
available evidence for which we could secure from reliable
sources. Consequently, after much deliberation and consideration,
it was decided to go forward on the basis of the available
evidence and nothing more. However, it must be known that
this was not a simple process, as it involved many difficult decisions
and much thought. In addition to the above mentioned difficulties,
there were also difficulties in obtaining the necessary
information and data required for the preparation of the
report. This was a long and arduous task, but it was finally
completed and the report was submitted to the appropriate
authorities.

Conclusion

The report has been prepared to meet the needs of the
Government of India.

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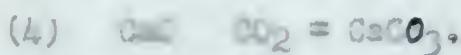
The report has been prepared to meet the needs of the Government of India.

At the temperatures required for suitable catalyzed reaction velocities the carbon monoxide is incompletely converted at the equilibrium composition when a stoichiometric amount of steam is used. To obtain a higher conversion of carbon monoxide and a purer hydrogen one or more of the following methods may be used:

- (1) Using steam in excess of the stoichiometric amount⁹
- (2) Removing carbon dioxide as rapidly as it is formed^{10,11}
- (3) Reacting in steps with carbon dioxide removal at the end of each step.^{2,3}

The effect of using excess steam is shown in Table I. If hydrogen of high purity is desired this process is not economical because of the very large quantities of steam required.

The carbon monoxide can be completely converted by removing carbon dioxide as the reaction proceeds. Calcium oxide is generally used for removing the carbon dioxide. Steam and carbon monoxide are passed over lime containing a catalyst of the type described above at a temperature below the dissociation temperature (1517° F.) of calcium carbonate. The carbon dioxide formed by the carbon monoxide conversion reacts with the lime to form calcium carbonate as follows:



For complete conversion, all of the carbon dioxide

the first time in history that the United States has been involved in a war without being attacked. The American people have been asked to support our troops in a conflict that they do not fully understand. We must remember that we are fighting for freedom and democracy, and that we are supporting our allies in their fight against terrorism. We must also remember that we are fighting for the safety of our own country and for the safety of our loved ones. We must stand together and support each other in this difficult time.

formed must be reacted with an equivalent molar quantity of lime, so that in the conversion process there must be some means of bringing unreacted lime in contact with the water gas and of discharging the calcium carbonate, which is heated to form calcium oxide again.

The effect of carrying out the conversion in stages with removal of carbon dioxide at the end of each stage is shown by the calculated values below, using one mol of steam in each stage and starting with one mol of carbon monoxide in the first stage.

Stage	Temperature °F.	Mol Carbon Monoxide Converted
1.	800	.75
2.	800	.221
3.	800	.026
		<u>.997</u>

It is seen that the steam consumption for a given degree of conversion of carbon monoxide is much less in a multi-stage process than in a single stage process.

De glijding vloog rechtstreeks naar achteren en landde op de grond.
Aan de voorzijde van de vliegtuigen was een grote
grote wieg voor spullen en een kleinere achteraan. De achter
kant van de vliegtuigen had een gelijmde houten achterwand
die de vliegtuigen mocht beschermen tegen de wind en
deze was ook voorzien van een achterste deur die
was om te kunnen open en sluiten. De achterste deur was
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De achterste deur was goed gesloten en was niet meer te
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openen.

Production of Hydrogen from Hydrocarbons and Steam

The reactions between saturated hydrocarbon gases, such as methane, ethane, or propane, and steam have been found an economical and convenient means of producing hydrogen. The saturated hydrocarbons are the principal constituents of natural gas, coke-oven gas and waste gas from petroleum cracking processes. Where cheap natural gas is available, processes utilizing the steam-hydrocarbon reactions are the most economical methods of producing pure hydrogen in large quantities.¹²

The reactions which occur are:



Reaction (6) may be considered as Reaction (5) followed by the water-gas reaction



These reactions are endothermic and must be carried out at elevated temperatures. In Figure 1, it can be seen that at temperatures above 1500° F. the equilibrium constant

$$K = \frac{(CO)(H_2)^3}{(CH_4)(H_2O)}$$

is large, so that at equilibrium the methane must be nearly completely converted,

Die politische Differenzierung zwischen den beiden Parteien ist nicht so groß wie die sozialen und geistigen Unterschiede zwischen ihnen. Die sozialen Unterschiede sind sehr groß, aber die politischen Unterschiede sind nicht so groß. Es gibt eine gewisse Übereinstimmung zwischen den beiden Parteien in Bezug auf die sozialen Unterschiede, aber es gibt auch Unterschiede. Die sozialen Unterschiede sind sehr groß, aber die politischen Unterschiede sind nicht so groß.

jein beigangs- und durch den Oberzähnen eine zentraleinheit bildet. Die Zähne sind nach der Art der Verankerung in die Zahnlücke zu unterscheiden. Im ersten Bereich befinden sich die sogenannten *freien* oder *lokalisierten* Zähne.

Catalysts must be used to give a practicable rate of reaction. German Patent No. 296,866 of 1912 proposed a catalyst of nickel or nickel oxides on a refractory support. The following material on catalysts for the hydrocarbon-steam reactions is quoted from the patent literature:

"Nickel alone even with the exclusion of chlorine and other catalyst poisons is not very active for the production of hydrogen by a reaction between steam and hydrocarbons at temperatures below 700° C.... by the addition of ... promoters (... cerium oxide, ... chromium oxide, ... aluminum oxide ...) the catalytic behavior of nickel in this reaction can be improved to the extent that the conversion of hydrocarbons into hydrogen becomes practicable at temperatures materially below 700° C.... The operation can be conducted ... at higher temperatures. ... Certain substances greatly decrease or even completely inhibit the activity of nickel catalysts for this purpose. Among such substances are the halogens, such as chlorine, and compounds of sulfur."¹³

"... a compound of nickel and chromium oxide such as nickel chromite is a more active catalyst than a mixture of nickel and chromium oxide."¹⁴

"The catalyst used is ordinarily a mixture of nickel or cobalt oxides with alumina or thoria ... "¹⁵

"Suitable catalysts for the production of hydrogen should

possess high activity and great physical strength, and should shrink very little at the operating temperature used. Oxides or metals of the iron group, admixed with aluminum oxide, form desirable catalyst. Calcium and magnesium oxides and silica may be added to secure catalysts of greater strength at high temperatures. Phosphoric acid with alumina and nickel oxide produces a very active catalyst which shrinks very little at high temperatures. A specially suitable catalyst is prepared from nickel oxides, magnesia and kaolin.¹⁶

The equilibrium compositions in the methane-steam reaction, starting with one mol of methane and two mols of steam, have been calculated for various temperatures and are given in Table II³ on a dry basis.

Table II

Equilibrium Compositions in The Methane-steam Reaction

Component	Percentage Composition					
	935° F.	1340° F.	1500° F.	1600° F.	1700° F.	1800° F.
H ₂	61	75.8	76.1	76.1	75.9	75.9
CO ₂	23	1.0	0.1	0.04	0.01	0.01
CO	4	17.2	19.1	19.7	20.3	20.7
SO ₂	12	6.0	4.7	4.2	3.8	3.4

klasse der öffentlichen Dienste durch den mittleren Beamtenstand
niedrig. Eine erheblich niedrigere Zahl der mittleren Beamten ist
im gleichen Zeitraum (die Bevölkerung wurde um 10 % größer), so
dass die Beamten pro 1000 Einwohner 1910 10,5 waren, 1920 11,5 und 1930
12,5. Die Abgrenzung zwischen dem mittleren und dem höheren
Beamten-Dienst ist in den drei Jahren 1910-1930 nicht sehr deutlich. Der Unterschied
in der Beamtenzahl zwischen mittlerem und höherem Beamtenstand
beträgt 1910 0,5, 1920 0,5 und 1930 0,5.

1993-1994-1995-1996-1997-1998-1999

From a study of equilibrium data for the hydrocarbon-steam reactions, it can be seen that the maximum yield of hydrogen can be obtained by one or more of the following methods:

- (1) Reacting at temperatures favoring the formation of carbon dioxide and using steam in excess of the stoichiometric amount
- (2) Reacting at temperatures favoring the formation of carbon dioxide and removing the carbon dioxide as rapidly as it is formed
- (3) Reacting at temperatures favoring the formation of carbon monoxide and then converting the carbon monoxide as previously described.

The processes using excess steam are not as economical and do not give as high conversion of hydrocarbons as other processes. The reaction is generally carried out using a 10 to 1 to 15 to 1 volume ratio of steam to hydrocarbon, temperatures below about 1300° F. and pressures of from 1 to 50 atmospheres. Although low pressures favor the conversion of hydrocarbons, high pressures may be used to reduce heat losses.^{17,18,19,20}

Processes based on the removal of carbon dioxide as rapidly as formed are described in the patent literature. The product from these processes contains at least two per cent methane.^{11,12} The author has found no references in the technical literature on the commercial application of these methods.

The processes involving the reaction of hydrocarbons with steam at temperatures above 1500° F. to form carbon monoxide, with the subsequent conversion of the carbon monoxide at temperatures below 900° F., are capable of producing hydrogen of high purity more economically than can other hydrocarbon conversion processes. A plant with a capacity of 13,000,000 cubic feet per day has been described.^{22,23}

A mixture of equal parts, by volume, of gas and steam, at atmospheric pressure, passes downward through vertical alloy-steel tubes packed with a catalyst of the nickel type. The tubes, about 25 feet long and 6 inches in diameter, are placed in two rows in a refractory-lined furnace and are supported at their tops. The furnace is heated by gas burning at the top of the furnace and between the rows of tubes.¹⁶ The natural gas and steam, flowing downward through the tubes at space velocities up to 300 volumes of hydrocarbon gas per hour per volume of catalyst, react nearly completely and leave the bottom of the tubes at about 1750° F. with about the

following composition:

Component	Per Cent (Dry Basis)
Hydrogen	73.
Carbon monoxide	15.
Carbon dioxide	10.
Methane	1.
Nitrogen	1.

After this reaction, more steam is added and the carbon monoxide is converted to carbon dioxide at about 250° F. by a catalytic water-gas reaction. The resulting gas mixture, containing about 78 per cent hydrogen, 20 per cent carbon dioxide, and 2 per cent unconverted methane and carbon monoxide, is then cooled with water in coke-packed towers, compressed to 750 pounds per square inch and scrubbed in a bubble tower with a monoethanolamine solution to remove carbon dioxide. The product has about the following composition:

Component	Per Cent
Hydrogen	35 - 47
Carbon monoxide	1.5 - 2.0
Methane	1 - 1.5
Nitrogen	0 - 1.5
Carbon dioxide	Trace.

A process for the production of pure hydrogen, utilizing the hydrocarbon-steam reaction with the subsequent conversion of carbon monoxide, has been developed.³ This process uses commercial propane as process material and as fuel.

Propane vapors, heated to about 700° F., are passed over bauxite or metallic oxide catalysts for the conversion of organic sulphur compounds to hydrogen sulphide. The vapor is then cooled and scrubbed with a caustic solution to remove the hydrogen sulphide.

The sulfur-free propane is mixed with steam and passed downward over the catalyst in the tubes of a Shapleigh²¹ furnace. This furnace consists of catalyst-filled nickel-chromium-iron alloy tubes placed vertically and supported at their tops in a refractory-lined shell. Gas burners are placed in the furnace tangentially to the walls so that the combustion gases are given a spiralling upward motion around the tubes and along the furnace walls. With this furnace, space velocities of about 600 volumes of hydrocarbon per hour per volume of catalyst are attained with temperatures above about 1600° F. in the reaction gases.

These reaction gases, cooled to about 700° F. with steam, are passed over a catalyst, at space velocities of 100 or more volumes of carbon monoxide and hydrogen per hour per volume of catalyst, for conversion of the carbon monoxide to carbon

dioxide. After this reaction the excess steam is condensed and the gases are cooled to about 100° F. and passed through a scrubber to remove carbon dioxide.

The carbon dioxide is absorbed by scrubbing with a solution of 15 to 20 per cent of monethanolamine in water. After scrubbing, the gas contains about one per cent of carbon monoxide, which is removed in two more stages of carbon monoxide conversion and carbon dioxide removal.

The hydrogen produced by this process has about the following composition:

Component	Per Cent
Hydrogen	99.968
Methane	0.015
Carbon dioxide	0.001
Carbon monoxide	0.001
Nitrogen	0.027
Oxygen	0.005 100.000

Year	Number of families	Number of children	Number of adolescents	Number of adults	Number of elderly
1970	1,000	1,000	100	100	100
1980	1,000	1,000	100	100	100
1990	1,000	1,000	100	100	100
2000	1,000	1,000	100	100	100
2010	1,000	1,000	100	100	100
2020	1,000	1,000	100	100	100
2030	1,000	1,000	100	100	100
2040	1,000	1,000	100	100	100
2050	1,000	1,000	100	100	100
2060	1,000	1,000	100	100	100
2070	1,000	1,000	100	100	100
2080	1,000	1,000	100	100	100
2090	1,000	1,000	100	100	100
2100	1,000	1,000	100	100	100

Conclusions

The hydrocarbon-steam process provides the most economical and convenient means of producing hydrogen in the United States. It has been developed to such an extent that it is used almost exclusively in new installations.²

Among the advantages of the process are: continuous and automatic operation resulting in minimum labor costs; high purity of hydrogen obtainable; and simplicity of mechanical design.

Consequently, given such low rates, it is unlikely that the observed changes in the number of individuals per hectare are due to increased mortality.

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